Macromol. Symp. ***143****, 45–63 (1999)*

Recent Developments in Photoinitiated Radical Polymerization

Christian Decker

Laboratoire de Photochimie Générale (UMR-CNRS N°7525)- Ecole Nationale Supérieure de Chimie de Mulhouse, Université de Haute-Alsace - 3, rue Werner – 68200 Mulhouse (France)

SUMMARY : This article presents the progress made in the development of high-speed photocurable resins and reports the performance of some novel radical-type photoinitiators, acrylate monomers and telechelic oligomers. The polymerization kinetics has been studied by real-time infrared spectroscopy, which records conversion *versus* time curves for reactions occurring in a fraction of a second. Phosphine oxides are among the most efficient photoinitiators and proved to be particularly well suited for the photocuring of pigmented systems and for solar-assisted polymerization. Acrylate monomers containing a heterocyclic oxygen in their structural unit exhibit an unexpectedly high reactivity. The introduction of an amino group in the chain of a telechelic acrylate-polyester causes a substantial acceleration of the polymerization process. In both cases, the increase in reactivity was attributed to the presence of labile hydrogen atoms which favor chain transfer reactions. The copolymerization of donor-acceptor monomer systems, like vinyl ether-maleate or vinyl ether maleimide, was shown to proceed readily upon UV irradiation, even in the absence of added photoinitiator. Light-induced polymerization was also used to crosslink rapidly polymers functionalized with acrylate or vinyl double bonds, namely acrylated polyisoprene and a styrene-butadiene block copolymer. The addition in small amounts (1 wt%) of a trifunctional thiol was found to speed up drastically the crosslinking polymerization, causing insolubilization of the thermoplastic elastomer to occur after a 0.1 s exposure.

Introduction

Light-induced polymerization is one of the most efficient processes for producing rapidly polymer materials having well-defined characteristics, in particular three-dimensional polymer networks. The use of radiation instead of heat to initiate the polymerization reaction affords a number of unique advantages, namely, very high reaction rates at ambient

CCC 1022-1360/99/$ 17.50+.50/0

temperature, low energy consumption, solvent-free formulation and spatio-temporal control of the polymerization. As a result, UV-radiation curing has experienced a sustained growth over the past decade, and it has found a large variety of industrial applications, mainly in the coating industry, photolithography, microelectronics and 3-D prototyping. Most of the research efforts have been focused on both the kinetics and mechanism of those high-speed crosslinking-polymerization reactions, and on the design of new photoinitiators, monomers and telechelic oligomers, best suited to producing polymers with tailor-made properties. The subject has been extensively covered in several textbooks and comprehensive review articles 1-9).

In the present paper, the progress recently made in a few of these areas will be outlined, and new potential applications of the UV-curing technology will be suggested. Special attention will be given to the basic chemistry which drives such ultrafast molecule to material transformations. Although crosslinked polymers can also be readily produced by photoinitiated cationic polymerization of multifunctional monomers 10), we will restrict our survey to radical-initiated polymerization which is by far the most widely used process in today's UV-curing applications.

Basic principle of photoinitiated crosslinking polymerization

Photocurable formulations are usually made of three basic components : a photoinitiator, a telechelic oligomer and a mono or multifunctional monomer. All three are essential to achieve a fast and extensive polymerization and produce a material showing the desired properties.

Most of the monomers do not generate free radicals with sufficiently high yields when they are exposed to UV light, either because they do not absorb this type of radiation, or because the excited molecules formed do not split into radical fragments. It is therefore necessary to use a photoinitiator which must absorb efficiently the incident light and produce very reactive radicals with high yields.

The physical properties of UV-cured polymers are mainly governed by the chemical structure of the telechelic oligomer which will constitute the backbone of the 3-D network. A large variety of acrylate end-capped polymers has been developed over the years to meet the specific demand of the ever-growing number of end-users. They differ primarily by their functionality (2 to 8), and their chemical structure (ester, urethane, ether, silicone,...). All these factors have been shown to control both the speed and the overall extent of the curing reaction [2,8)].

Monomers need to be introduced in UV-curable formulations to reduce their viscosity and make them suitable for industrial processing, specially in thin film applications (coatings, adhesives, photoresists). As the monomer may contain up to 4 acrylate double bonds in its molecule, it will act as a crosslinking agent, thus affecting the polymerization kinetics and the final properties of the cured material as well.

The performance of some newly developed photoinitiators, telechelic oligomers and monomers will be discussed, mainly with respect to their efficiency and reactivity in UV-curable formulations. Besides the widely used acrylate-based resins, we will also examine donor-acceptor systems, such as maleate/vinyl ether and maleimide/vinyl ether combinations, which undergo a fast radical initiated polymerization upon UV exposure. Finally, the photoinduced crosslinking of functionalized polymers in the solid state will be discussed briefly, as it constitutes an effective and simple method to generate rapidly three-dimensional polymer networks.

Novel radical photoinitiators

The photoinitiator (PI) plays a key role in light-induced polymerization for it controls both the reaction rate and the depth of cure profile within the sample. The rate of initiation (r_i) is directly proportional to the quantum yield of formation of initiating species (Φ_i) and to the incident light intensity (I_0), and it varies exponentially with the photoinitiator concentration [PI] :

$$r_i = \Phi_i \, I_0 \, [1 - \exp(-\varepsilon \, l \, [PI])$$

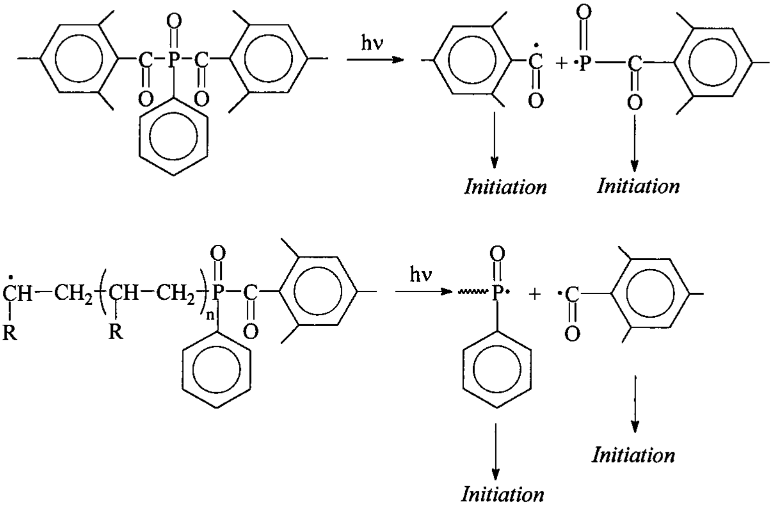
where l is the sample thickness and ε the photoinitiator absorptivity.

The most efficient photoinitiators belong to the class of aromatic carbonyl compounds that undergo homolytic C-C bond cleavage upon UV exposure, with formation of two radical fragments. Among the various radical-type photoinitiators developed so far, morpholinoketones (MoK) and bisacylphosphine oxides (BAPO) from Ciba Specialty

Chemicals, exhibit superior efficiency for the UV-curing of both clear and pigmented coatings 11). Figure 1 shows the polymerization profiles, recorded by real-time infrared (RTIR) spectroscopy, for a clear polyurethane acrylate resin exposed to UV radiation in the presence of different photoinitiators at a concentration of 2 wt%. Several factors are considered to be responsible for the better performance of bisacylphosphine oxides :

- a greater absorptivity in the near UV range, where the mercury lamp has its strongest emission (365 nm),
- a faster photolysis than most radical photoinitiators,
- a large initiation quantum yield,
- the high reactivity of the benzoyl and phosphinoyl radicals.

Moreover, as a result of the difunctional character of BAPO, 4 initiating radicals are produced per molecule destroyed, after absorption of two photons 12) :



Because their absorption spectra expand up to the visible region, MoK and BAPO proved to be particularly efficient photoinitiators to polymerize up to 100 μm thick pigmented coatings 11,12). With these photoinitiators, the UV-curing of colored systems, which was so far restricted to printing inks (≤ 5 μm thickness), can now be extended to paints and lacquers, thus opening a new field of applications to the UV-curing technology.

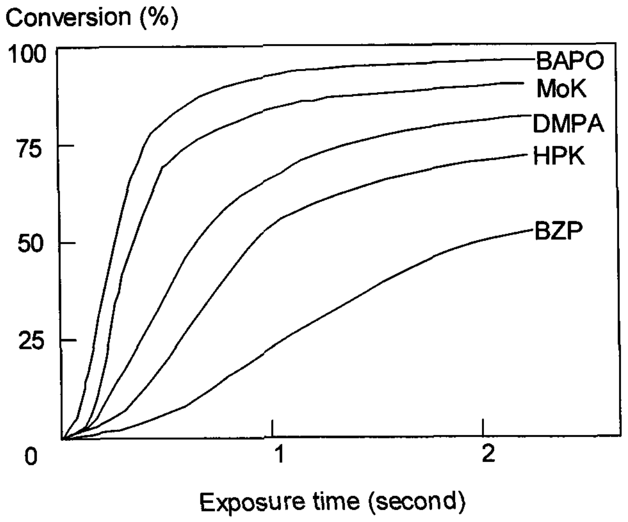


Fig. 1 : Influence of the photoinitiator (2 wt%) on the polymerization of a polyurethane-acrylate. Light-intensity : 12 mW cm^{-2}. BZP : benzophenone ; HPK : hydroxyphenyl-ketone ; MoK : morpholinoketone ; DMPA : dimethoxyphenylacetophenone ; BAPO : bisacylphosphine oxide

A distinct advantage of phosphine oxide photoinitiators is that they undergo a fast photolysis to generate non-colored products. Figure 2 shows the PI decay profiles recorded by real-time UV spectroscopy for a polyurethane-acrylate exposed to UV radiation in the presence of a BAPO or a morpholinoketone photoinitiator. The twice faster destruction of phosphine oxides is one the reasons of their higher initiation efficiency, as the rate of initiation is directly related to the rate of the PI photolysis.

Phosphine oxides are ideal candidates to perform photoinduced frontal polymerization for they fulfil the two main requirements : high light absorbance and fast photobleaching 13). At the beginning of the exposure, the initiating radicals are mainly generated in the top layer because of the limited penetration of UV radiation. As the absorbing photoinitiator is being destroyed, the incident light penetrates deeper into the sample and the polymerization front moves progressively from the surface to the bulk of the sample. By using BAPO as photoinitiator, a deep-through cure of a few centimeter thick acrylate sample was achieved within less than one minute of UV irradiation to give a transparent glass.

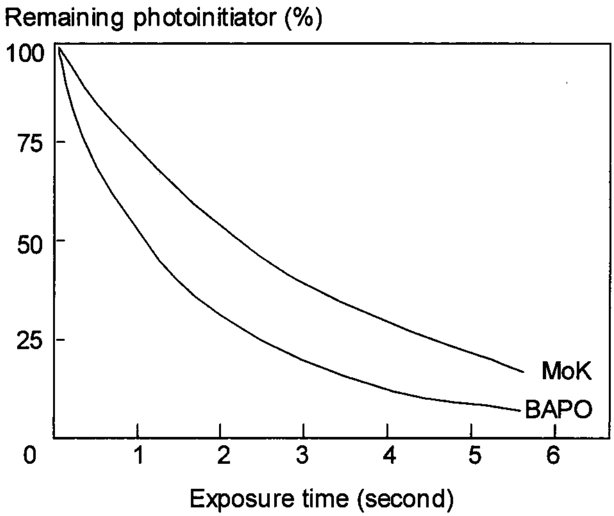


Fig. 2 : Photoinitiator loss profile recorded by RTUV spectroscopy at 300 nm for BAPO and at 322 nm for morpholino ketone (MoK), upon UV exposure of a polyurethane-acrylate.

Such frontal polymerization was also carried out in a very economical way by a simple exposure to sunlight for up to 5 minutes. This solar technology was successfully applied to produce glass laminates and glass composites, as the BAPO photoinitiator has the distinct advantage of absorbing effectively the UV radiation transmitted by mineral glass. For these novel applications, different types of telechelic oligomers and monomers have been selected :

- an aliphatic polyurethane-acrylate, associated to a monoacrylate monomer, to produce upon solar curing the low-modulus elastomer needed as safety glass intercalate ;
- an aromatic polyether-acrylate, associated to a di- or triacrylate monomer, to produce a hard and tough composite material.

Figure 3 shows the polymerization profiles of these two types of photocurable resins upon outdoor exposure at noon by clear sky. As expected from functionality number and molecular mobility considerations, the polyurethane-based resin polymerizes slower but more extensively than the polyether-based resin.

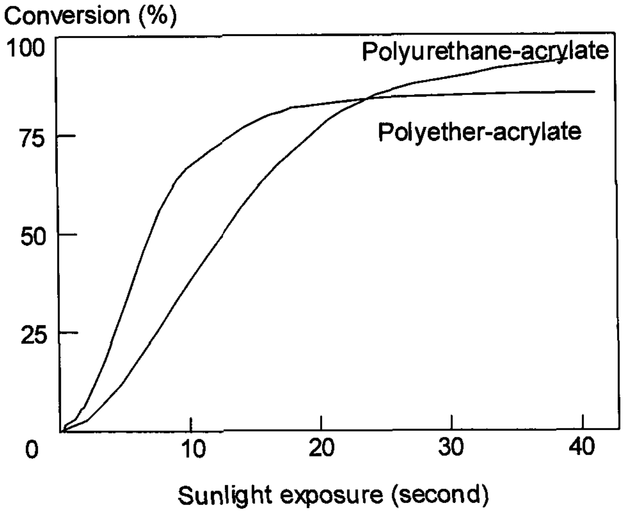


Fig. 3 : Polymerization profile of telechelic acrylate oligomers exposed to sunlight in the presence of a BAPO photoinitiator.

Deep through curing of adhesives and composite materials can also be carried out readily by exposure to a laser beam [14)], in particular the 365 nm emission of the Ar^+ laser, at which wavelength BAPO shows a distinct absorption peak [12)]. One of the unique advantages of using lasers to initiate the polymerization, besides the rapidly, is that the solidification of a precise area can be performed on order at a great distance. For instance, two pieces of an assembly located on a satellite can be instantly bound together on order, by simply firing the laser.

Photopolymerization of acrylate systems

Most of the photosensitive resins used in UV-radiation curing applications are made of acrylate monomers and telechelic oligomers, because of the high reactivity of the acrylate double bond. The rate constant of the propagation reaction (k_p) is on the order of 15000 $l\ mol^{-1}\ s^{-1}$ for acrylate monomers, compared to less than 1000 $l\ mol^{-1}\ s^{-1}$ for methacrylate monomers [15)]. The basic characteristics of photocured polymers depend from the chemical structure and functionality of both the monomer and the oligomer, and on their relative amounts. One of the prime objectives in UV-curing chemistry is to create new monomers and oligomers that will undergo fast and extensive polymerization to form crosslinked polymers showing the desired properties for a given application.

Highly reactive acrylate monomers

The monomer used to lower the formulation viscosity is a key ingredient, for it affects both the polymerization kinetics and the properties of UV-cured polymers. An increase in the monomer functionality is usually speeding up the reaction, but at the expense of the final conversion, because of early gelation and vitrification of the crosslinked polymer. Introducing a heterocyclic oxygen into the structural unit of a monomer was found to cause a substantial acceleration of the polymerization, which still proceeds until near completion$^{16)}$. The formulas of the various monoacrylates studied are given in Figure 4. They were mixed, in a 1/1 weight

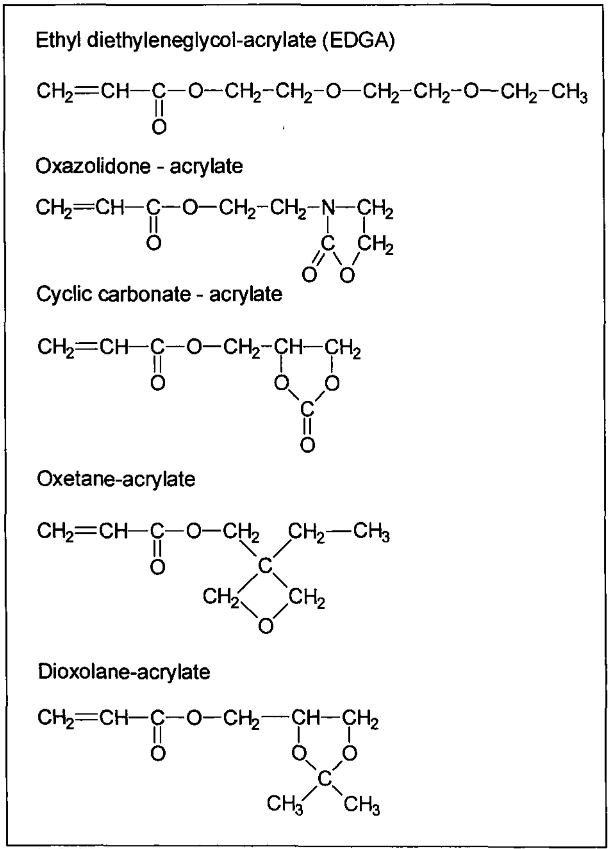


Fig. 4 : Formulas of highly reactive monoacrylate monomers

ratio, with an aliphatic polyurethane-diacrylate oligomer (M_n = 1300) and exposed to UV radiation in the presence of a benzil diketal photoinitiator (5 wt%). Figure 5 shows the conversion *versus* exposure time curves recorded by infrared spectroscopy for the various formulations. These monomers can be classed in the following order of increasing reactivity :

Ether < oxetane < dioxolane < oxazolidone < cyclic carbonate

The reasons of the enhanced reactivity brought upon by the heterocyclic structure are not fully understood so far. They seem to be related to the presence of labile hydrogens which favor chain transfer reactions, thus making these monomers to behave like crosslinking agents. Indeed, unlike usual monoacrylates, these heterocyclic monoacrylates were found to become totally insoluble when exposed to UV light in the presence of a photoinitiator. Their hydrogen donor character has been demonstrated by photopolymerization experiments carried out with benzophenone as photoinitiator 9). While conventional mono or diacrylate, did not undergo significant polymerization under those irradiation conditions, these heterocyclic acrylates were found to homopolymerize rapidly. Another advantage of using these monomers as reactive diluents is that they impart both hardness and flexibility to the UV-cured polymers 16), which also exhibit a strong resistance to organic solvents, chemicals and weathering.

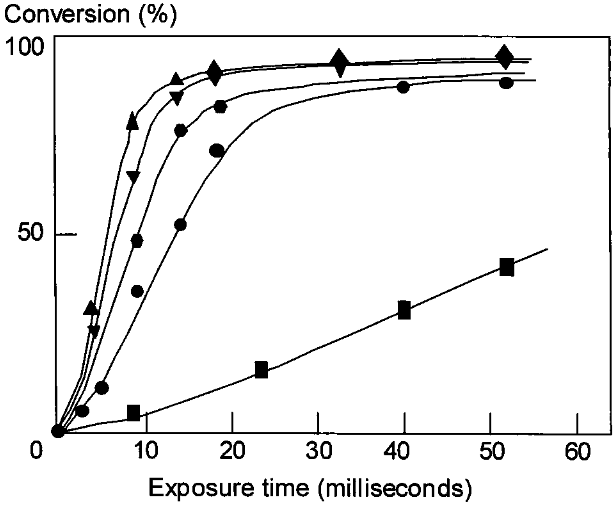


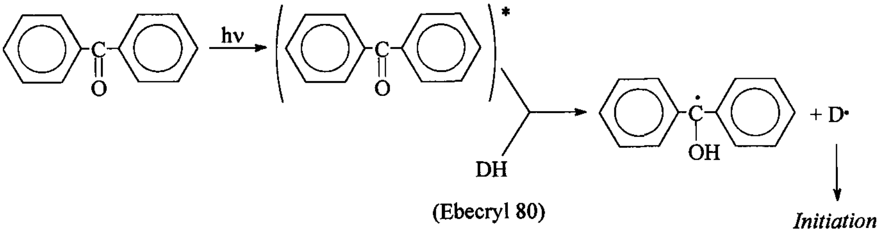
Fig. 5 : Light-induced copolymerization of a polyurethane-diacrylate with various acrylic monomers in the presence of air. I = 500 mW cm^{-2}. [DMPA] = 5 wt%. Monomer/oligomer weight ratio = 1. ▲cyclic carbonate, ▼oxazolidone, ◆dioxolane, ●oxetane, ■ether.

Telechelic acrylate oligomers

The reactivity of a UV-curable resin depends primarily on the functionality and chemical structure of the acrylate functionalized oligomer. The viscosity of the liquid oligomer, which varies with its molecular weight, controls the kinetic chain length as it affects both the propagation and the termination rate constants [17)]. In a UV-curable polyurethane-acrylate resin, the slowing down effect of viscosity was found to be more pronounced on k_t than on k_p [18)]. Consequently, the polymerization rate did increase as the initial viscosity of the formulation was increased from 50 to 1000 mPa s by lowering the amount of reactive diluent. As crosslinking polymerization proceeds, the polymer radicals bound to the network are loosing their reptation mobility. The termination step becomes then controlled by the rate at which the polymer chains are growing, as shown by the linear relationship between k_t and k_p [M] [17)].

Aromatic groups are often introduced in the oligomer chain to obtain hard and glassy polymers showing a remarkable resistance to chemicals, heat and scratching. They may however have a detrimental effect on the polymerization kinetics for two main reasons : (i), aromatic groups reduce the initiation rate because they absorb deep UV radiation (inner filter effect) and (ii), they cause a premature ending of the polymerization because of vitrification. Increasing the sample temperature is an effective way to achieve a more complete cure in high-modulus crosslinked polymers and thus reduce the amount of unreacted acrylate double bonds. This can be done by simply increasing the intensity of the photon flux (irradiance), which causes the sample temperature to rise, the heat of the reaction being then evolved in a shorter time. Temperatures up to 100°C have been recorded upon UV-curing of acrylate coatings under intense illumination and a concomittant increase in final degree of conversion has been observed [19)]. A direct consequence of this effect is that the physical characteristics of photocured polymers will depend on the irradiation conditions (light intensity, initial temperature), as well as on the formulation reactivity (higher temperatures will be reached in more reactive systems).

If desired, the reactivity of UV-curable acrylic resins can be increased by introducing labile hydrogens in the oligomer chain. A typical example is the amino-polyester tetra-acrylate (Ebecryl 80 from UCB) which was found to polymerize faster and more completely than a typical polyester-hexaacrylate (Ebecryl 830), specially in combination with an oxazolidone-acrylate monomer [20)]. Figure 6 shows the polymerization profiles of the two formulations UV-irradiated in the presence of a benzil diketal photoinitiator. Here again, the hydrogen donor character of Ebecryl 80 was demonstrated by the fact that, unlike Ebecryl 830, it polymerizes readily when exposed to UV light in the presence of benzophenone, a photoinitiator which produces only free radicals by hydrogen abstraction :



The main interest of this telechelic oligomer, when used in association with H-abstraction type photoinitiator, is that it does not require the addition of tertiary amines. Besides their bad odor, these liquid compounds are known to lower the elastic modulus of photocrosslinked polymers, because of their plasticizing effect and their propensity to induce chain transfer reactions. Moreover, the presence of a readily oxidizable amino group will contribute in reducing the inhibitory effect of oxygen on such radical-induced polymerization.

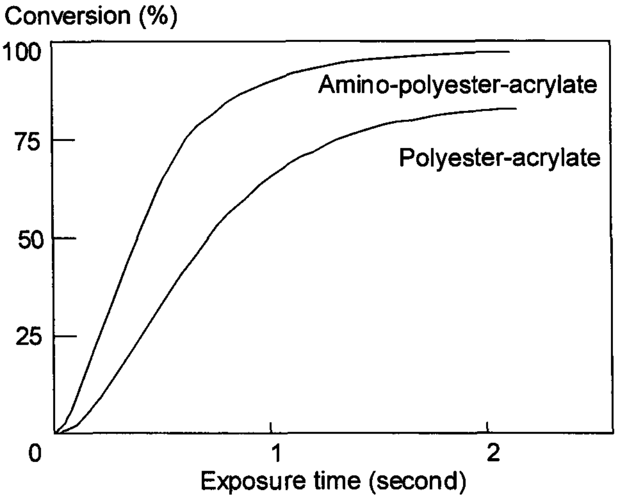


Fig. 6 : Influence of the telechelic oligomer structure on the reactivity of a UV-curable acrylate resin. [Irgacure 651] = 3 wt%.

Photopolymerization of donor-acceptor systems

A current trend in UV-curing chemistry is to develop non-acrylate resins that would be as reactive but more friendly to the environment than the widely used acrylate monomers which show a strong odor and may cause eye and skin irritation. A promising system investigated recently is based on the copolymerization of an electron-donor monomer, like vinyl ethers, with an electron-acceptor monomer, like maleates or maleimides.

Maleate-vinyl ether system

Vinyl ether (VE) do not homopolymerize in the presence of photogenerated free radicals, because of their electron-rich double bond. They may however undergo copolymerization with monomers having an electron-poor double bond, like unsaturated esters 21,22). Figure 7 shows a typical polymerization profile recorded by RTIR spectroscopy for a 1/1 mixture of a divinyl ether and a dimaleate (MA) exposed to UV radiation in the presence of a phosphine oxide photoinitiator. Whatever the monomer feed ratio, the two monomers were found to polymerize at the same rate, which reached its maximum value for a stoichiometric composition 23). The quantity of maleate polymerized is always the same as that of vinyl ether polymerized, which implies the formation of an alternating copolymer. The total amount of residual unsaturation in the UV-cured VE-MA copolymer is the lowest for the stoichiometric composition (~20% of the original amount). It can be reduced by increasing the light intensity, and thus the temperature, or by adding small amounts of a cationic photoinitiator (triarylsulfonium salt).

A kinetic study by RTIR spectroscopy has shown that the copolymer is formed by homopolymerization of a donor-acceptor complex, and not by a cross-propagation mechanism 23). The fact that a photoinitiator-free VE/MA mixture undergoes copolymerization (Fig.7), although at a much lower rate because of its very low UV absorbance, argues in favor of a mechanism based on a donor-acceptor complex. This type of UV-curable resins were found to be less sensitive to oxygen inhibition than acrylate resins, thus allowing a fast-drying of thin coatings in the presence of air.

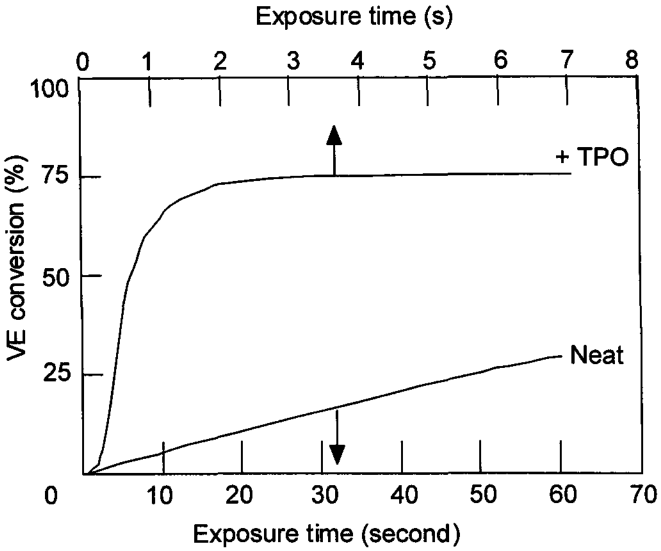
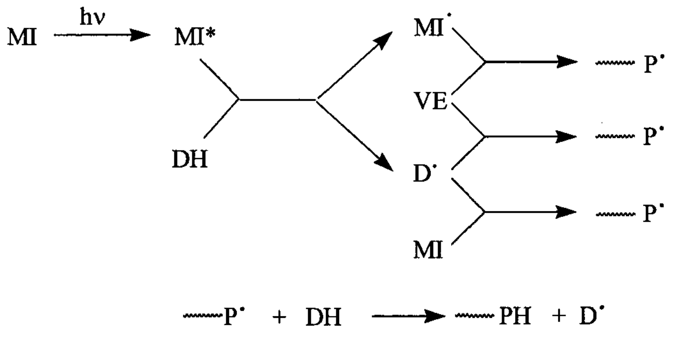


Fig. 7 : Polymerization profile of the vinyl ether function upon UV exposure of a VE/MA stoichiometric mixture. I = 60 mW cm^{-2}.

Maleimide-Vinyl ether system

A marked increase in reactivity was observed by associating the vinyl ether monomer to a N-substituted maleimide (MI). A series of such photoinitiator-free UV curable systems consisting of a couple of electron-donor/electron-acceptor monomers has been recently studied by S. Jönsson et al. 24). Their polymerization rate was shown to be as high as that of acrylate resins containing a radical-type photoinitiator. In these photoinitiator-free resins, UV radiation is absorbed mainly by the maleimide monomer to form excited molecules which are capable to abstract hydrogen atoms from either one of the two monomers.

Like with the maleate/vinyl ether system, the two monomers were found to disappear at similar rates upon UV exposure, to reach nearly 100% conversion within a few seconds and formation of an alternating copolymer 25). Figure 8 shows how similarly the degrees of conversion of the VE and MI monomers vary with the exposure time, for a stoichiometric mixture of hydroxybutyl vinyl ether and hydroxypentyl maleimide. Hydrogen abstraction plays a key role in the polymerization efficiency by intervening both in the initiation step and in the propagation step through a chain transfer reaction. The latter is responsible for branching and insolubilization of the polymer.



The observed effect of the monomer feed composition on the reaction kinetics suggests that chain propagation proceeds *via* an acceptor-donor complex. One of the remarkable features of this type of radical-induced polymerization, besides the absence of any added photoinitiator, is its low sensitivity toward oxygen inhibition. A few micron thick films made of a mixture of bismaleimide and divinyl ether monomers have thus been photocured readily in the presence of air. Moreover, the fact that polymerization is accompanied by a fast photobleaching of the light-absorbing maleimide monomer allows thick samples to be cured by frontal polymerization.

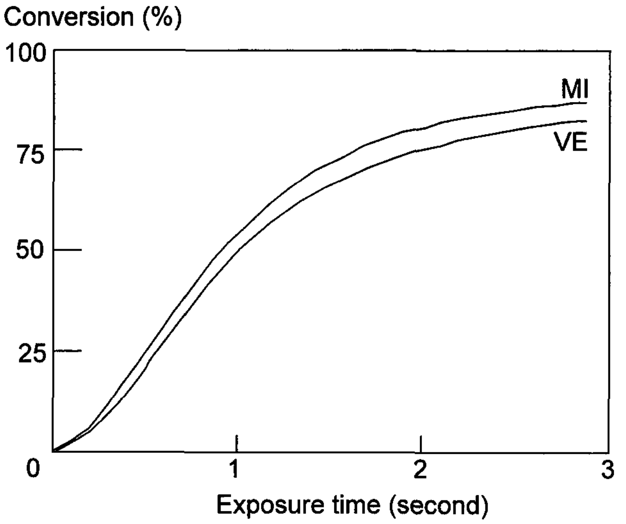


Fig. 8 : Polymerization profiles recorded by RTIR spectroscopy upon UV exposure of a photoinitiator-free maleimide/vinyl ether combination (MI/VE = 1).

N-substituted alkyl maleimides were also shown to act as monomeric photoinitiators by inducing effectively the polymerization of acrylate monomers upon UV-exposure 26). Based on its distinct characteristics, this type of photocurable system is expected to find its main applications as protective coatings, photoresists and quick-setting adhesives and composites.

Photocrosslinking of functionalized polymers

Besides transforming a liquid resin into a solid polymer, UV-radiation can be used to induce the polymerization of reactive groups in a solid polymer to achieve insolubilization and to modify its physical properties. The functional group can be located either on an incorporated monomer or/and on the polymer chain itself. Photoinitiated radical polymerization has proved very effective to crosslink readily different types of polymers, in particular acrylated natural rubber 27) and styrene-butadiene thermoplastic elastomers 28).

Acrylate functionalized polyisoprene

Epoxidized polyisoprene was treated by acrylic acid to generate pendent acrylate groups on the polymer chain. As many as 80% of the grafted double bonds did polymerize after a 10 s UV exposure in the presence of a morpholino-ketone photoinitiator ([MoK] = 2 wt%). The insoluble polymer formed shows a low degree of swelling (DS) in organic solvents (DS = 3 in chloroform), which indicates the formation of a relatively tight polymer network. The in-chain amylene double bonds of polyisoprene were found to also contribute to the network formation by copolymerizing with the acrylate double bonds 27).

The crosslinking reaction can be markedly accelerated by introducing small amounts of a di- or triacrylate monomer which acts as a reactive plasticizer. The acrylate double bonds from both the functionalized rubber and the monomer undergo a fast homopolymerization and copolymerization with the amylene double bond, with formation of a hard and insoluble polymer, as shown in Figure 9. A 0.1 s UV exposure proved to be sufficient to achieve an effective crosslinking and transform the low-modulus elastomer into a high-modulus thermoset polymer. By using as reactive plasticizer a monomer that polymerizes by a cationic mechanism, such as epoxides, two interpenetrating polymer networks have been formed simultaneously upon UV-irradiation in the presence of both a radical and a cationic photoinitiator. A potential application of these highly sensitive dry photoresists is in microlithography where they could serve to produce well-contrasted relief images upon UV or laser exposure.

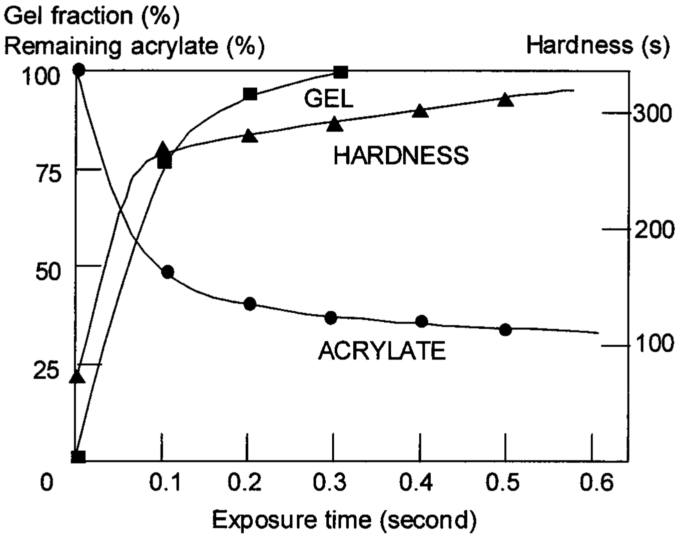


Fig. 9 : Photocrosslinking of acrylated polyisoprene in the presence of a triacrylate monomer. Light intensity : 600 mW cm^{-2}.

Vinyl functionalized polybutadiene

By contrast to polyisoprene, which does not undergo any crosslinking upon UV exposure in the presence of a photoinitiator, polybutadiene can be "photovulcanized" readily at ambient temperature, because it contains a few vinyl double bonds formed by 1-2 polymerization of butadiene. Thermoplastic elastomers, polystyrene-*block*-polybutadiene-*block*-polystyrene (SBS from SHELL), have thus been made more resistant to organic solvents and heat, while improving their adhesive strength 28,29). In the presence of a phosphine photoinitiator, insolubilization was achieved after a 2 s UV-exposure when about 10% of the vinyl groups have reacted, which corresponds to 17 double bonds (or crosslinks) per polybutadiene chain . Therefore, the tridimensional polymer network has a very loose structure, a conclusion confirmed by the high value of the degree of swelling measured in the photocured SBS (DS = 32). The hardness of the polymer increased upon UV exposure, but the irradiated sample remained flexible and retained its elastomeric character.

In an attempt to increase the crosslinking efficiency, a diacrylate-polyphenoxy oligomer was introduced in the SBS rubber at a concentration of 20 wt%. A 0.2 s exposure proved to be sufficient to induce the polymerization of 14% of the vinyl groups and 3% of the butene-2 double bonds 28). At the same time 70% of the acrylate groups had polymerized, most of it by copolymerization with the SBS double bonds. The additional crosslinks account for the lowering of the swelling ratio (DS = 10) and the increase of the Persoz hardness (from 80 to 200 s) of the UV-cured film, which remained highly flexible.

An even more effective photocuring of the SBS rubber was achieved by using a trifunctional thiol as crosslinking agent. Under intense illumination, the thiol/ene polymerization 30) proceeds within a fraction of a second by a step growth addition mechanism to yield an insoluble polymer network. Both the butene and the vinyl double bonds of polybutadiene are attacked by the thiyl radicals, which are 10 times more reactive toward the pendent vinyl groups. A remarkable feature in this system is that the thiol content can be reduced down to 1 wt%, the same concentration as the photoinitiator (Lucirin TPO). It can be seen in Figure 10 that insolubilization of SBS occurs much faster than in the neat rubber, and even faster than in the sample containing 20 wt% of the diacrylate oligomer. Lowering the thiol content is of a great interest because it not only reduces the cost of the formulation, but it also lessens some of the disadvantages associated with the use of sulfur compounds, in particular the bad smell. In this respect, it should be emphasized that the photocured polymer has no unpleasant odor anymore because essentially all of the thiol groups have reacted and are chemically bonded to the polymer network.

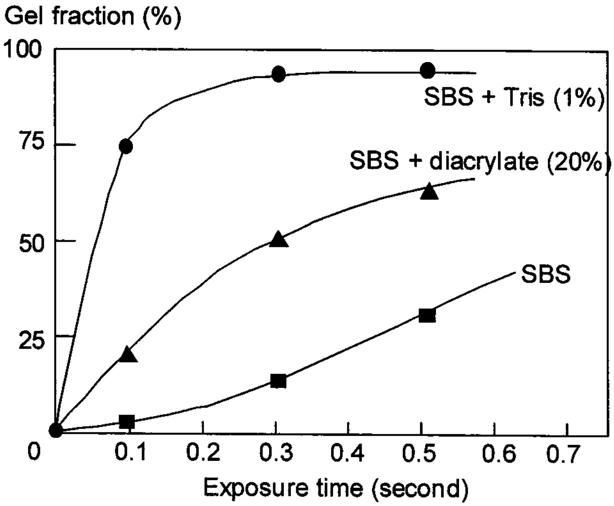


Fig.10 : Photocrosslinking of an SBS thermoplastic elastomer UV-irradiated neat or in the presence of a diacrylate or a trifunctional thiol monomer. [Lucirin TPO) = 1 wt%. I = 600 mW cm^{-2}.

Conclusion

Photoinitiated radical polymerization of multifunctional monomers, telechelic oligomers and functionalized polymers remains one of the most effective methods to produce highly crosslinked polymer networks. By using light to activate the chain reaction, the polymer chemist is capable to transform quasi-instantly a liquid molecule into a solid material, selectively in the illuminated areas. Because of its unique advantages regarding process facility, spatio-temporal control and product quality, the UV-curing technology has found its major openings in the coating industry, the graphic arts and in microelectronics.

Significant progress has been achieved in recent years with the development of very efficient photoinitiators and highly reactive monomers and oligomers. Polymer materials showing specific, tailor-made properties can thus be precisely designed for a particular end-use. With the development of laser-curable resins, photopolymerization has entered into new areas of applications, such as holography, stereolithography and optoelectronics. Based on present and foreseeable achievements, the prospects of UV-radiation curing look rather bright, and further progress can be expected to be achieved in the near future by acquiring a better knowledge and control of such ultrafast crosslinking polymerization reactions.

Acknowledgements. *The authors wishes to thank his coworkers at the Polymer Photochemistry Laboratory, Drs. S. Biry, D. Decker, T. Nguyen Thi Viet, K. Zahouily, Ms. C. Bianchi and F. Morel.*

References

1). S.P. Pappas (Ed.), *UV-curing Science and Technology*, **2**, Technology Marketing Corp., Stamford CT (1985)

2). C.E. Hoyle and J.F. Kinstle (Eds*), Radiation Curing of Polymeric Materials*, ACS Symp.Seri. **417**, (1990)

3). P.X.T. Oldring (Ed), *Chemistry and Technology of UV and EB Formulation for Coatings, Inks and Paints*, **1-4**, SITA Technology, London (1991)

4). J.P. Fouassier and J.F. Rabek (Eds*), Radiation Curing in Polymer Science and Technology*, Plenum Press, New York (1992)

5) J.P. Fouassier, *Photoinitiator, Photopolymerization and Photocuring*, Hanser, Munich 1995

6) A.B. Scranton, C.N. Bowman, R.W. Peiffer, *Photopolymerization. Fundamentals and Applications*. ACS Symp.Series 673, Amer.Chem.Soc. (Washington) 1997

7). J.G. Kloosterboer, *Adv.Polym.Sci.*, **84**, 1 (1988)

8). C. Decker, *Progr.Polym.Sci.* **21**, 593 (1996)

9). C. Decker, in *Materials Science and Technology*, Vol 18, HEH Meijer (ed) VCH Publish, Weinheim (1997) p.615

10) J.V. Crivello, *Adv.Polym.Sci.* **62**, 2 (1984)

11) K. Dietliler in ref.2, Vol 3, p.91 (1991)

12) K. Dietliker, D. Leppard, T. Jung, M. Köhler, A. Valet, U. Kolzack, P. Rzadek, G. Rist, *Proc.RadTech Asia Conf. Yokohama*, (1997), p.292

13) C. Decker, *Polym. Intern.* **45**, 133 (1998)

14) C. Decker in ref 3, Vol 5, p.147 (1994)

15) A.M. Van Herk, *J.Macromol.Sci.Rev.* **C.37**, 633 (1997)

16) K. Moussa, C. Decker, *J.Polym.Sci., Polym.Chem.Ed.* **31**, 2197 (1993) and in ref 4 Vol 3, p.33 (1993).

17) K.S. Anseth, C.M. Wang, C.N. Bowman, *Polymer*, **33**, 3243 (1994) and *Macromolecules* **27**, 650 (1994)

18) C. Decker, B. Elzaouk, D. Decker, *J.Macromol.Sci., Pure Appl.Chem.* **A33**, 173 (1996)

19) C. Decker, D. Decker, F. Morel in ref.6, p.63

20) C. Decker, B. Elzaouk, *J.Appl.Polym.Sci.* **65**, 833 (1997)

21) T. Korkubo, S. Iwatsuki, Y. Yamashita, *Macromolecules*, **1**, 482 (1968).

22) S.C. Lapin, J.J. Schouten, C.K. Noren, E.J. Mosehovic, *Proc.RadTech Europe Conf.* 1993, p.502

23) C. Decker, D. Decker, *Polymer* **38**, 2229 (1997)

24) S. Jönsson, P.E. Sundell, J. Hultgreen, D. Sheng, C.E. Hoyle, *Progr.Org.Coat.* **27**, 107 (1996)

25) F. Morel, C. Decker, S. Jönsson, S.C. Clark, C.E. Hoyle, Polymer (in press)

26 C.E. Hoyle, S.C. Clark, S. Jönsson, M. Shimoses, *Polymer*, **38**, 5695 (1997)

27) C. Decker, T. Nguyen Thi Viet, H. Le Xuan, *Europ.Polym.J.* **32**, 559 (1996)

28) C. Decker, T. Nguyen Thi Viet, *Polym.Mater.Sci.Eng.* 74, 327 (1996).

29) M. Dupont, N. De Keyser, *Proc.RadTech Europe Conf.* Maestricht, 1995, p.174

30) A.F. Jacobine in ref.4, Vol 3, p.219